Commonwealth of Virginia
Department of General Services
Division of Consolidated Laboratory Services
Richmond, Virginia

Method Detection Limit Revision 2 (40 CFR 136 App B)

Definition and Procedure for the Determination of the Method Detection Limit, Revision 2 [40 CFR 136 Appendix B] EPA 821-R-16-006, https://www.epa.gov/cwa-methods					
The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.					
Facility Name:_____VELAP ID_____ Assessor Name:_____Analyst Name:_____Inspection Date_____					
Relevant Aspect of Standards	**Method Reference**	**Y**	**N**	**N/A**	**Comments**
Records Examined: SOP Number/ Revision/ Date _____ Analyst:_____ Method: _____ Matrix: _____ Analyte: _____ Instrument(s): _____ MDL Date: _____					
1. Were all sample processing steps used by the laboratory included in the determination of the MDL?	Scope and Application				
2. NOTE: The MDL is not applicable to methods where low-level spiked samples cannot be prepared. An MDL may be based on method blanks for gravimetric methods. (Refer to method for additional detail.)	Scope and Application				
3. Were samples prepared from a clean reference matrix spiked with a known and consistent quantity of the analyte?	Scope and Application				
ESTIMATION OF THE INITIAL MDL					
4. Was the INITIAL MDL estimated using one or more of the following (indicate the selection(s)) _____ a) The mean determined concentration plus 3x the standard deviation of a set of method blanks _____ b) The concentration value that corresponds to an instrument signal-to-noise ratio in the range of 3 to 5 _____ c) The concentration equivalent to three times the standard deviation of replicate instrumental measurements of spiked blanks _____ d) That region of the calibration where there is a significant change in sensitivity, i.e, a break in the slope of the calibration _____ e) Instrumental limitations _____ f) Previously determined MDL	1(a) through 1(f)				
DETERMINATION OF THE INITIAL MDL					
5. NOTE: The initial MDL is used when the laboratory does not have adequate data to perform the Ongoing Annual Verification specified in Section (4), typically when a new method is implemented or if a method was	2				

rarely used in the last 24 months					
6. Was a spiking level of 2-10 times the estimated MDL selected? NOTE: Spiking levels in excess of 10x the estimated detection limit may be required for analytes with very poor recovery NOTE: Careful planning at this stage so that the spiking level ALSO meets the requirements of 2016 TNI V1M4 1.5.2.2 will enable the laboratory to use the EPA MDL procedure to satisfy 2016 TNI V1M4 1.5.2.	2(a)				
7. Were a minimum of 7 spiked samples and 7 method blanks processed through all steps of the method?	2(b)				
8. Were samples used for the MDL prepared in at least 3 batches on three separate calendar dates?	2(b)				
9. Were samples used for the MDL analyzed on three separate calendar dates?	2(b)				
10. NOTES: ○ Preparation and analysis may be on the same day. ○ Existing data may be used, if compliant with the requirements for at least 3 batches and generated within the last 24 months. ○ The most recent available data for method blanks and spiked samples must be used. Only data associated with gross failures with documentation for rationale (ex: instrument malfunctions, mislabeled samples, cracked vials) may be removed. ○ The same prepared extract may be analyzed on multiple instruments. ○ A spiked sample and a method blank sample may be analyzed in the same batch, but are not required to be.	2(b), 2(b)(iii)				
11. If multiple instruments will be assigned the same MDL, sample analyses must be distributed across all instruments. Was each instrument represented with a minimum of two spiked samples and two blank samples prepared / analyzed on different days?	2(b)(i), 2(b)(ii), 2(d)				
12. Spiking level evaluation: Did every result from spiked samples meet the method qualitative identification criteria? Did every result from spiked samples provide a numerical result greater than zero? If the answer to either question is NO, the spiked samples used for initial MDL determination must be repeated at a higher concentration.	2(c)				
13. Were all computations made as specified in the analytical method and expressed in the method-specified reporting units?	2(d)				
14. Was the **MDL_s (the MDL based on spiked samples)** computed as follows?	2(d)(ii)				

$MDL_s = t_{(n-1,\ 1-\alpha=0.99)} * S_s$ Where MDL_s = MDL based on spiked samples $t_{(n-1,\ 1-\alpha=0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom. (See Table 1, below; 3.143 when n=7) S_s = sample standard deviation of the replicate spiked sample analyses					
15. Was the **MDL_b (the MDL based on method blanks)** computed as follows? <u>If none of the method blanks give numerical results for an individual analyte</u>, the MDL_b does not apply. NOTE: A numerical result includes both positive and negative results, including results below the current MDL, but not results of "ND" [not detected] commonly observed when a peak is not present in chromatographic analysis. --- OR --- <u>If some (but not all) of the method blanks for an individual analyte give numerical results</u>, set the MDL_b equal to the highest method blank result. If more than 100 method blanks are available, set MDL_b to the level that is no less than the 99th percentile of the method blank results. For "n" method blanks where n ≥ 100, sort the method blanks in rank order. The (n * 0.99) ranked method blank result (round to the nearest whole number) is the MDL_b. [Refer to published method for a mathematical example.] --- OR --- <u>If all of the method blanks for an individual anayte give numerical results</u>, then calculate the MDL_b as: $MDL_b = \bar{x} + t_{(n-1,\ 1-\alpha=0.99)} S_b$ Where MDL_b = MDL based on method blanks $\bar{x}$ = the mean of the method blank results $t_{(n-1,\ 1-\alpha=0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom. (See Table 1, below; 3.143 when n=7) S_b = sample standard deviation of the replicate method blank analyses NOTE: If the mean of the blanks is <0 (i.e., a negative number), substitute 0 for the mean. NOTE: If 100 or more method blanks are available,	2(d)(iii)(A) 2(d)(iii)(B) 2(d)(iii)(C)				

as an option, MDL_b may be set to the concentration that is greater than or equal to the 99th percentile of the method blank results, as described in Section (2)(d)(iii)(B)					
16. Was the greater of MDL_s or MDL_b selected as the initial MDL?	2(e)				
ONGOING DATA COLLECTION					
17. Was ongoing data collected as follows? During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked samples on each instrument, in separate batches, using the same spiking concentration used in Section 2 [initial MDL calculation]. NOTE: If any analytes are repeatedly not detected in the quarterly spiked sample analyses or do not meet the qualitative identification criteria of the method the spiking level should be adjusted upward. (See 3(c).) NOTE: It is not necessary to analyze additional method blanks together with spiked samples; include all of the routine method blanks analyzed with each batch during the course of (routine) sample analysis.	3(a)				
18. Did ongoing data collection ensure that at least seven spiked samples and seven method blanks were completed for the annual verification? NOTE: If only one instrument is in use, a minimum of seven spikes are still required, but they may be drawn from the last two years of data collection.	3(b)				
19. At least once per year, was the spiking level re-evaluated? NOTE: If more than 5% of the spiked samples do not return positive numerical results that meet all method qualitative identification criteria, the spiking level must be increased and the initial MDL re-determined following the procedure in Section 2.	3(c)				
20. NOTE: If the method is altered in a way that can be reasonably expected to change its sensitivity, re-determine the initial MDL according to Section 2 and restart the ongoing data collection.	3(d)				
21. If applicable, was the following addressed if a new instrument was added? If a new instrument is added to a group of instruments whose data are being pooled to create a single MDL, analyze a minimum of two spiked replicates and two method blank replicates on the	3(e)				

new instrument. • If both method blank results are below the existing MDL, then the existing MDL_b is validated. • Combine the new spiked sample results to the existing spiked sample results and recalculate the MDL, as in Section 4. • If the recalculated MDL_s does not vary more than the factor specified in Section 4(f) of this procedure, then the existing MDLs is validated. • If either of these two conditions is not met, then calculate a new MDL following instructions in Section 2.					
ONGOING ANNUAL VERIFICATION					
22. Was the MDL_s and MDL_b re-calculated at least once every thirteen months from the collected spiked samples and method blank results from the last 24 months using the equations in Section 2?	4(a)				
23. For the MDL_s, was all data generated within the last 24 months, but only data with the same spiking level, included in the recalculation? NOTE: Include the initial MDL spiked samples, if the data were generated within 24 months. NOTE: Use only data associated with acceptable calibrations and batch QC. Include all routine data with the exception of batches that are rejected and the associated samples reanalyzed. NOTE: Only documented instances of gross failures may be excluded from the calculations. NOTE: If the laboratory believes the sensitivity of the method has changed significantly, then the most recent data available (i.e., data collected after the change) may be used, maintaining compliance with the requirement for at least 7 replicates in three batches on three separate days (per Section 2(b).)	4(b), 4(c), 4(d)				
24. For the MDL_b, were all method blank results from the last 24 months used? NOTE: The laboratory has the option to use only the last six months of method blank data or the 50 most recent method blanks, whichever criteria yields the greater number of method blanks. Indicate the option used by the laboratory: _____ _____	4(e)				

25. Was the verified MDL the greater of the MDL_s or MDL_b?	4(f)				
26. Was the verified MDL within 0.5 to 2.0 times the existing MDL, and did fewer than 3% of the method blank results have numerical results above the existing MDL? _____ If so, the existing MDL may be left unchanged at the option of the laboratory. If not, adjust the MDL to the new verified MDL.	4(f)				
27. NOTE: Refer to the published method for determination of the MDL for a specific (sample) matrix.	Addendum				
28. Were documentation requirements met? _____ The prep date, analysis date, and instrument for each analysis was available for evaluation of MDL compliance. _____ The analytical method used for MDL determination was specifically identified by number or title. _____ The MDL for each analyte was expressed in the method reporting units. _____ Data and calculations used to establish the MDL can be reconstructed upon request. _____ The sample matrix used to determine the MDL was identified with the MDL value. _____ The mean spiked and recovered analyte levels were documented with the MDL. _____ The rationale for removal of outlier results, if any, was documented and maintained on file with the results of the MDL determination.	Documentation and Procedure				
Notes/ Comments:					

THIS SCHECKLIST IS AN INTERVIEW AND/OR DATA REVIEW TOOL USED BY ASSESSORS AND IS NOT TO BE CONSIDERED AS A SUBSTITUTE FOR REQUIREMENTS OF THE PUBLISHED METHOD. CHECKLISTS ARE SUBJECT TO CHANGE. PLEASE NOTIFY DCLS IMMEDIATELY BY EMAIL OF ANY IDENTIFIED ERRORS OR OMISSIONS. (Lab_Cert@dgs.virginia.gov)

Table 1: Single-Tailed 99th Percentile *t* Statistic

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, 0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
16	15	2.602
32	31	2.453
50	49	2.405
80	79	2.374
100	99	2.365

A Student's T table with values to 100 and a calculation tool for values >100 is located on the VELAP toolbox webpage at www.dgs.virginia.gov/dcls (Choose Laboratory Accreditation, then Toolbox), or use this LINK.

QUICK CHECKLIST (see full checklist for supporting details and full compliance):

____ All sample processing steps
____ Initial: 7 samples + 7 blanks minimum
    ____ Prep/Testing on at least 3 days
    ____ Testing uses all instruments
____ Determined MDL is greater of MDL_S and MDL_B
____ Ongoing: 7 samples (same spike conc) + 7 blanks minimum over year
    ____ Collected each quarter samples were run (2 determinations per instrument, separate batches)
    ____ Spiking level increased (and initial repeated) if >5% of spikes fail to return positive numerical results / meet all identification criteria
    ____ Uses all data for same level spike and all blank data (or can use last 6 months or 50 most recent, whatever is greater)
____ Annual re-calculation (<13 months) and evaluation of MDL_S and MDL_B using most recent 24 months' data
    ____ Verified correct Student's T value used
    ____ MDL verified as within 0.5 to 2.0 times the existing MDL with <3% of blanks above existing MDL, or initial is repeated
____ For simultaneous 2016 TNI Standard Compliance of all of Section 1.5.2: Spike level at or below LOQ
____ Supporting data available as specified